Article

Chinese Science Bulletin

Materials Science

October 2013 Vol.58 No.30: 3698–3703
doi: 10.1007/s11434-013-5995-8

The structural changes of blood pyropolymers and their beneficial electrocatalytic activity toward oxygen reduction

GUO ChaoZhong[1], CHEN ChangGuo[1*] & LUO ZhongLi[2]

[1] *College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, China;*
[2] *College of Basic Medical Sciences, Molecular Medicine and Cancer Research Center, Chongqing Medical University, Chongqing 400046, China*

Received March 26, 2013; accepted May 15, 2013; published online July 12, 2013

There is a growing interest in designing more effective fuel cell cathode catalyst precursors. Here the partial pyrolysis of animal bloods has been used to produce the blood pyropolymers, which are an intermediate substance between a polymer and carbonaceous material. These pyropolymers were yielded by carbonization process below 600°C. The structural changes in the pyropolymers were characterized by X-ray diffraction, and their formation was checked by micro-IR spectra, thermogravimetric and differential thermal analysis. Their potential electrocatalytic properties were evaluated using the linear sweep voltammetry in the O_2-saturated KOH solution. It is found that the process of pyropolymer formation began about 200°C and completed around 500°C. The change of particle phase depends on the formation of the pyropolymers, but has no effect to their internal carbon structures which are controlled by pyrolysis process only. Meanwhile, it is confirmed that the crystalline phases in the pyropolymers can exist at the surface of heat-treated materials. It can be also found that the carbon materials are active toward oxygen reduction and their activity is associated with the carbonization level. Our study will stimulate the designers to design the highly active catalysts by using native blood pyropolymers as the precursors.

animal blood pyropolymer, structural change, electrocatalytic activity, oxygen reduction reaction, catalyst precursor

Citation: Guo C Z, Chen C G, Luo Z L. The structural changes of blood pyropolymers and their beneficial electrocatalytic activity toward oxygen reduction. Chin Sci Bull, 2013, 58: 3698–3703, doi: 10.1007/s11434-013-5995-8

It is well-known that the general performance of fuel cells has been directly controlled by the oxygen reduction reaction (ORR) at the cathode [1]. The use of the catalyst consisting of platinum and a carbon support is the most effective method to accelerate the slow kinetic behavior of the ORR. However the platinum's scarcity and high cost is the critical issue that limits and hinders the rapid development and large-scale application of this technology [2,3]. Thus, there has been an increasing demand for the development of alternative catalysts that contain far less or no noble metals, free from resource limitation and cost inflation [4–6]. Since Jasinski firstly reported the ORR electrocatalysis of cobalt phthalocyanine in alkaline solution [7], various novel materials have been explored for reducing or replacing the Pt-based catalysts, especially for the carbon-based materials [8–17]. In recent years, several research groups have reported the heat-treated carbon materials containing nitrogen formed by carbonizing heme-containing proteins such as catalase [18] and hemoglobin [19–22]. A good activity and high powder density were also obtained from these materials, and yet it was indispensable to specifically emphasize that further study would be also required to improve the ORR activity and their stability.

The animal blood proteins are abundantly available and inexpensive; especially the pig blood protein, being from the meat industry that produces more than 200 million tons of meat every year worldwide, is thrown away as waste [19]. The animal bloods, including huge amounts of different bioproteins such as hemoglobin and myoglobin, should be thoroughly investigated due to their potential for preparing

*Corresponding author (email: cgchen@cqu.edu.cn)

the ORR catalyst. Unfortunately, there is no systematic study on the pyrolysis of blood proteins until now. It is necessary to investigate the carbonization behavior of various proteins. Maruyama et al. [22] reported the two-step carbonization process of hemoglobin from bovine blood in 2008. The substance prepared in the first heat-treatment step was designated as a precursor for the catalyst. Most recently, it has been recognized that the substance obtained by thermal treatment of a polymer material below 600°C is usually an intermediate between the polymer and carbon material because of its incomplete carbonaceous phase generation and could be called a pyropolymer [22]. However, the pyropolymer has not yet been studied in detail because its structure is extremely complex. A few investigations have recently been done, in which the characteristics of the pyropolymer were exploited to produce novel catalytic materials [17,23].

In this work, we investigated the formation of animal blood pyropolymers and their structural change that benefit electrochemical oxygen reduction activity in alkaline solution. It is found that the formation of the carbon matrix coupled with the crystalline phase change in the pyropolymer and its formation process was almost accomplished at about 500°C. Different animal blood proteins showed the similar formation behavior and catalytic activity based on the same and limited carbonization process. An increase in the pyrolysis temperature could promote the active centers inside the pyropolymer, resulting in the enhancement of the ORR activity. In addition, the internal carbon structure of pyropolymers is independent of the phase change, but their ORR catalytic mechanism needs to be studied further.

1 Materials and methods

1.1 Chemicals and materials

The animal bloods, including pig blood (PB), chicken blood (CB), duck blood (DB) and goose blood (GB), were supplied by Food Testing Center of Chongqing Bureau of Quality and Technology Supervision, and human blood (HB) was obtained from Chongqing University Hospital. All these bloods were used as received, without further purification. All other chemicals were of analytical grade from Chongqing Chemical Reagent Co., China.

1.2 Carbon materials preparation

All animal bloods were firstly oven-dried at 80°C for 12 h to remove inclusive moisture and then were mechanically milled for about 30 min to obtain the dried blood powder. After that, they were directly carbonized in a tube furnace at different pyrolysis temperature for 2 h under the N_2 atmosphere with a flow rate of 1 L min^{-1}, and then the furnace was naturally cooled to the ambient temperature. For convenience, the pyropolymer obtained from PB at 500°C is hereafter called PB500, and others are called like it. In order to explore the effect of crystalline phases on the carbon material, the PB500 was treated by ultrasound in pure water for 1 h, which is hereafter called PB500U. Besides, the DB, CB and GB dried powders were pretreated with dissolution in pure water by ultrasound to eliminate the soluble substances, and then they were carbonized in the same manner, which are hereafter called DB500AU, CB500AU and GB500AU, respectively.

1.3 Physicochemical characterization

Thermogravimetric and differential thermal analysis (TG/DTA) of PB powder was carried out on a Shimadzu differential thermal analyzer (DTG-60H, Japan) under N_2 flowing. The TG/DTA measurements were recorded from room temperature to 600°C with a ramp rate of 10°C min^{-1}. The X-ray diffraction (XRD) measurements were performed for characterizing the structure of different carbon materials using X-ray diffractometer by Shimadzu XRD-6000 (Japan) with Cu Kα radiation (λ = 1.54 Å) at the scan rate of 4° min^{-1}. FT-IR spectra were recorded (4 cm^{-1}, 64 scans) in reflection mode using a microscopic FT-IR spectrophotometer (Nicolet iN10, USA) equipped with attenuated total reflectance (ATR) accessory. The morphology of PB500 material was characterized by scanning electron microscopy (SEM) on a TESCAN instrument (VEGA 3 LM, Czech Republic) with a high voltage of 20 kV.

1.4 Electrochemical measurements

The linear sweeping voltammetry (LSV) was performed on CHI660A electrochemical workstation (USA) with conventional three-electrode system consisted of a catalytic thin-film working electrode, a ring-shaped Pt wire counter electrode and a standardized Hg/HgO reference electrode. The working electrode was a glassy carbon electrode (GCE, Φ = 5 mm) covered with a thin layer of Nafion-impregnated material. Typically, the thin-film electrode was prepared as follows: 5 mg of carbon material was dispersed in the solution (50 μL ultrapure water and 50 μL of 0.5 wt% Nafion/isopropanol) and ultrasonically blended for 20 min. A 10 μL of this ink was dropped on the GCE surface by using a pipette. The catalytic activity for ORR was evaluated by LSV curve in 0.1 mol L^{-1} KOH solution saturated by O_2. LSV was collected by scanning the potential from 0.3 down to –0.7 V at the scan rate of 5 mV s^{-1}.

2 Results and discussion

2.1 TG/DTA curves of PB dried powder

Figure 1 shows the result of TG/DTA for PB dried powder. It can be observed that a small change starts at about 30°C to reach a plateau near 150°C, which leads to a weight loss

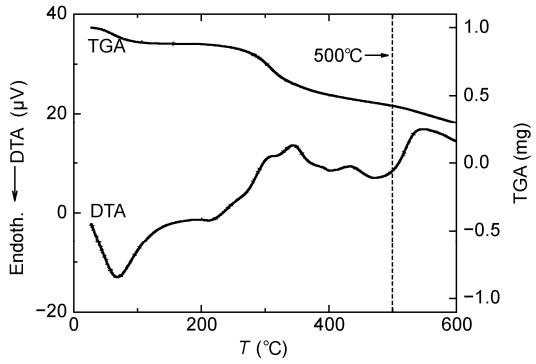

Figure 1 The TG/DTA curves of PB dried powder.

of 11.8% due to the removal of residual water adsorbed. At the same time, this change exactly corresponds to a large and symmetrical endothermal peak at 68.5°C appearing at the DTA curve. The following wave starts at about 200°C to reach a plateau near 500°C, which indicates that the pyrolysis process begins around 200°C. Here some complicated thermal changes are expected to occur and reflected on the DTA curve because the PB is not a simple compound, although those irregular peaks might be partially caused by the dynamic character of the TG/DTA measurement. However, it is convinced that the formation of several weak endothermal peaks displaying on the DTA curve as well as a weight loss of about 45.2% on the TGA curve might be mainly attribute to the decomposition of various amino acids within the PB. Based on the previous reports, it is anticipated that the carbonized procedure of single bioprotein is accomplished at about 500°C and the internal structure of low-temperature carbon materials absolutely shifts from the aliphatic to the aromatic carbon checked by ^{13}C NMR spectra [22]. For this reason, here a reasonable speculation is put forward that the formation process of PB pyropolymer will be completed at 500°C.

2.2 The structural change of PB pyropolymer and its ORR activity

Figure 2 shows the XRD patterns of heat-treated carbon materials obtained from pyrolysis of PB on the temperature of 100 to 900°C. It is observed that a large board peak at 2θ = 21° appears at 300°C, which indicates the existence of amorphous substances. While the pyrolysis temperature is between 300 and 700°C, a large amount of crystalline phases are obviously observed and the amorphous phase also appears with another board diffraction peak at 2θ = 25° (graphite 002). The change of amorphous phase also demonstrates that the carbonized process is being gradually accomplished with the increment of temperature. Furthermore, a set of sharp peaks at 28.28°, 40.44°, 50.08°, 58.52°, 66.30° and 73.64°, which could be assigned to cubic crystalline phase KCl, and another two weak peaks at 31.62° and 45.32° could be attributed to face-centered cubic crystalline phase NaCl. These phases might be formed through crystallization based on the pyrolysis process and it is notable that the degree of crystallinity can be promoted by further pyrolysis. Nevertheless, the crystallinity is limited with the heat-treated temperature beyond 500°C and the intensity of diffraction peaks is also reduced, which proves that the proposed speculation that the PB pyropolymer formation could be completed at 500°C to a certain degree. Besides, the most remarkable fact is the appearance of another amorphous phase at $2\theta = 44°$ (graphite 101) when the temperature is over 800°C. The two amorphous phases including C (002) and C (101) could be usually observed for activated carbon [24]. This indicates that the carbon structure within the pyropolymer might also be modified by further pyrolysis process, such as the increasing of graphitization degree.

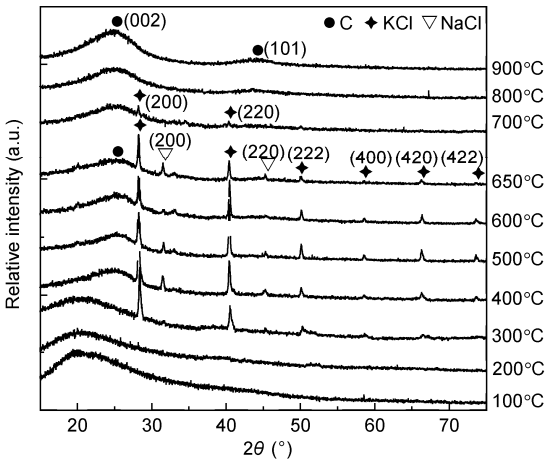

Figure 2 XRD patterns of PB carbon materials formed at 100 to 900°C.

In order to obtain more evidence in support of the speculation, the micro-infrared spectroscopy was used to characterize the surface of carbon materials formation at 100 to 500°C. As can be seen in Figure 3, the bonds depicted in the frequency range from 4000 to 600 cm^{-1} can be assigned as follows: 2960 cm^{-1} observed at under 400°C is due to antisymmetric C–H stretching formed in saturated carbon atom;

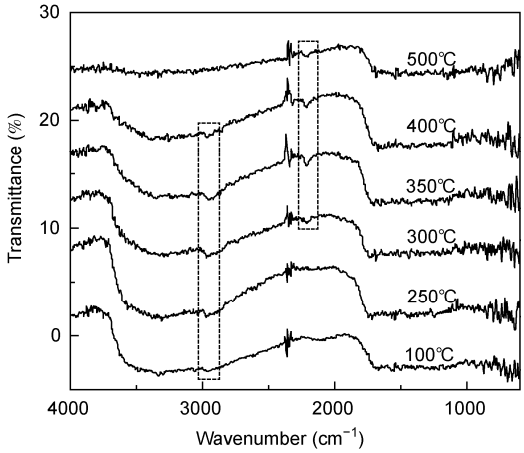

Figure 3 Micro-IR spectra of PB pyropolymers formed at 100 to 500°C.

2210 cm^{-1} corresponds to the C≡C stretching mode while the pyrolysis temperature is not less than 300°C; and the wide peak located between 3650 and 3200 cm^{-1} represents the O–H and N–H stretching, which originated from decomposition of amino acids containing in blood protein before thoroughgoing carbonization. Besides, an interesting phenomenon is also displayed on the micro-IR spectra, in which a rapid deterioration for groups including C–H, O–H and N–H occurs until at 500°C practically. Therefore, these results provide enough information to support the proposed supposition.

Based on the results of structural characterization, here we would like to find out the relationship between ORR catalytic activity and structural change in order to develop the novel function for PB pyropolymer. Figure 4 demonstrates the LSV curves of carbon materials obtained from different pyrolysis temperature in 0.1 mol L^{-1} KOH solution saturated by O_2. The onset potential for ORR (E_{onset}) together with cathodic oxygen reduction current (I_{pc}) was here chosen as the parameters for evaluating the electrocatalytic activity toward ORR. It is noticeable that the E_{onset} has shifted from –0.18 to –0.06 V and I_{pc} has increased from 0.07 to 0.16 mA. In addition, the peak potential for ORR (from (a) to (f)) also increases sharply with the increment of pyrolysis temperature from 300 to 800°C. It must be pointed out that the transformation from the pyropolymer to the catalyst may be carried out while the temperature is beyond 600°C. However, these results indicate that the carbonization level could play a critical role in improving the ORR catalytic activity and it is not associated with the crystalline phase change. Although the reason for this activity enhancement is unclear, the formation of ORR-active centers for PB pyropolymer should be enhanced at higher temperature. In addition, the overpotential slopes of the LSV curves also become larger, which could be explained by the negative influence of pure polarization resistance in pyropolymer materials. Thus, we can reasonably think that this PB pyropolymer could function as a promising candidate for further preparation of the ORR catalyst.

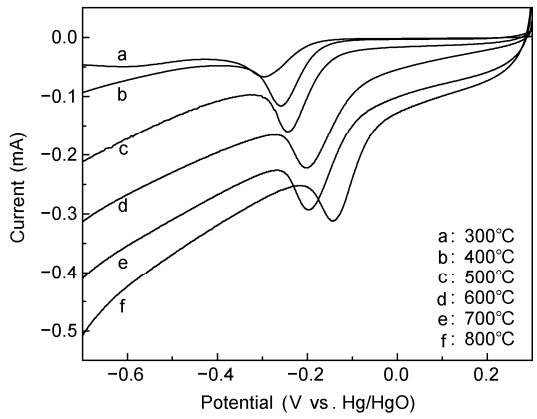

Figure 4 LSV curves of PB carbon materials produced at 300 to 800°C in 0.1 mol L^{-1} KOH solution saturated by O_2 at the scan rate of 5 mV s^{-1}.

2.3 The structural changes in other blood pyropolymers and their ORR activity

On the basis of the confirmed speculation, other four kinds of animal bloods, including DB, CB, GB and HB, were also chosen for pyrolysis in the same manner in order to verify whether the identical structure would be acquired. At first, we discussed the results of TG/DTA for these animal bloods and the similar data with the PB are also obtained, which are the pyropolymers formation process being accomplished at 500°C (not shown here). After doing this, we used the XRD spectra for characterizing the carbon materials from other animal bloods, as indicated in Figure 5. It can be observed that the cubic crystalline KCl phase has been still found clearly, but its relative content indicates a growing tendency from DB500 to PB500 under the same pyrolysis process. Furthermore, the crystalline phase NaCl does not exist in other blood pyropolymers except for the PB pyropolymer. After the PB pyropolymer was undergone the ultrasound treatment in pure water for 1 h, all the crystalline phases almost disappeared but the amorphous phases remained, suggesting that the existence of KCl phase did not influence the carbon structure of blood pyropolymers, and the produced crystalline KCl should be attached on the material surface merely, which was directly supported by analysis of SEM image from PB500 in Figure 6.

Another problem which has been drawn our attention is that animal blood pyropolymer was the most propitious to function as the catalyst precursor or candidate applied in fuel cells technology. Therefore, the ORR catalytic activity of different animal blood pyropolymers was evaluated by LSV curves, as shown in Figure 7. A result beyond our expectation has emerged which displays the similar ORR activity with the E_{onset} of –0.10 V. However, there are little differences in the peak potential for ORR and I_{pc} for the five carbon materials. This phenomenon may be ascribed to the complicated internal structure and compositions contained inside different blood pyropolymers. Besides, the catalytic

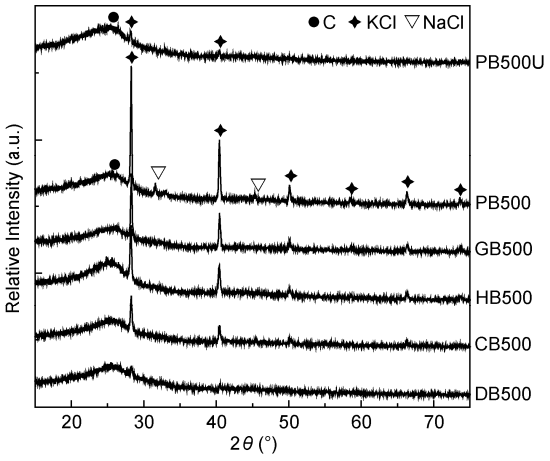

Figure 5 XRD patterns of the pyropolymers formed by pyrolysis of five animal bloods at 500°C.

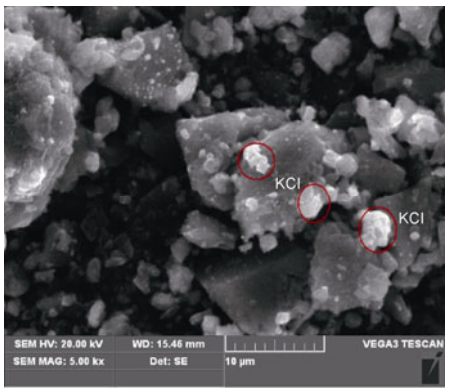

Figure 6 SEM image of the obtained PB500 carbon material.

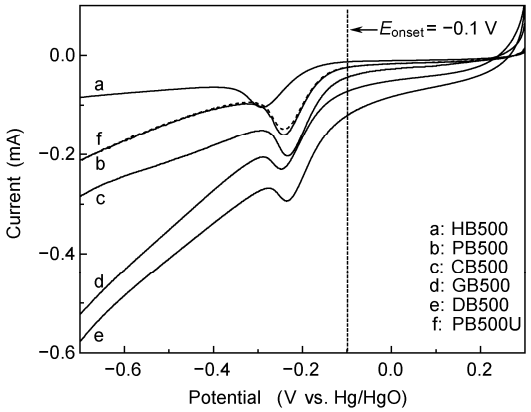

Figure 7 LSV curves of the pyropolymers from five animal bloods in 0.1 mol L^{-1} KOH solution saturated by O_2 at the scan rate of 5 mV s^{-1}.

activity of PB500U is almost the same as that of PB500, indicating that the catalytic activity has not been influenced whether or not the crystalline KCl is existed in carbon materials. Thus, it is undeniable that these pyropolymers are effective candidates for ORR catalysts.

For penetrating into acquaintance of the effect of KCl phase, the original three dried animal blood coagulations with dispersion in ultrapure water were treated by ultrasound. Figure 8 shows the XRD results of DB, CB and GB

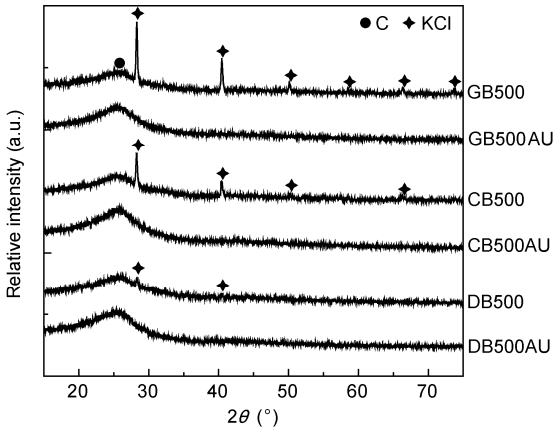

Figure 8 XRD patterns of the pyropolymers formed by pyrolysis of DB, CB and GB before and after dissolution of soluble substances at 500°C.

before and after dissolution of soluble substances. It is observed that except for the amorphous phase C (002), other crystalline phases do not occur for DB500AU, CB500AU and GB500AU. This may indicate that the dissolution of soluble substances containing in primary coagulations does not influence the carbonization process of bloods, though it results in losing the possibility of forming the crystalline phases. Furthermore, the phase C (101) could not be observed at the carbon materials whether or not they were treated by ultrasound. It further makes clear that the carbon structure of blood pyropolymers is controlled by pyrolysis process and has nothing to do with the existence of crystalline phases.

3 Conclusions

The structural change in several animal blood pyropolymers has been studied by comparing XRD patterns and then the relationship between their ORR activity and pyrolysis process has also been intensively researched. We found that the ORR activity of PB pyropolymer was enhanced with the increment of pyrolysis temperature but its crystallinity was restrained beyond 500°C. We confirmed that the formation process of animal blood pyropolymers was accomplished at 500°C from the results obtained by TG/DTA, XRD and micro-IR data. It was also found that the phase change of the pyropolymers did not influence their own carbon structures but were controlled by pyrolysis process, indicating that the carbon structures were not related to the crystalline phases whether they existed or not. These pyropolymers could be used as the effective ORR catalysts in alkaline solution, but the further enhancement of the ORR activity would be achieved by improving the pyrolysis procedure. More investigations should be performed to understand the ORR mechanism for these pyropolymers and to further improve these carbon-based catalysts.

This work was supported by the National Natural Science Foundation of China (21273292) and the Fundamental Research Funds for the Central Universities (CDJXS12220002). Dr. Luo ZhongLi was supported by the Natural Science Foundation Project of Chongqing (CSTC 2011BB5134), and the National Natural Science Foundation of China (81101417).

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